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NONSILVER, LIGHT-SENSITIVE PHOTOGRAPHIC ELEMENTS

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This invention is related to nonsilver photographic elements and more particularly to nonsilver bleachout and printout elements for photographic reproduction processes.

Photographic silver halide elements for printout processes are known in the art. Nonsilver photographic elements for printout processing are desired.

It is, therefore, an object of our invention to provide nonsilver photographic elements that are valuable for producing photographic copies by a printout or a bleachout process.

Another object is to provide a nonsilver printout or bleachout element comprising a support coated with a mixture of at least one pyrylium and/or at least one thiapyrylium salt, and an image promoting compound, preferably dispersed in a water-insoluble, water-permeable binder material.

Another object is to provide nonsilver printout or bleachout elements of our invention which produce images of various colors including substantially neutral colored dye images by using the appropriate pyrylium and/or thiapyrylium salt(s) in making the element.

Another object is to provide a printout or a bleachout process for producing a nonsilver image in our photographic element comprising the step of exposing such element to a light image, and when desired the step of stabilizing the image by washing the exposed element in water.

Still further objects will be apparent from the following specification and claims.

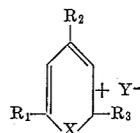
These and other objects are accomplished according to our invention. In its simplest form our printout or bleachout elements comprise a suitable support coated with a light-sensitive mixture comprising at least one pyrylium and/or at least one thiapyrylium salt, and an image promoting compound. In a preferred embodiment of our invention, the light-sensitive mixture is dispersed in a water-insoluble water-permeable binder material.

The color of the dye image formed in our element upon printout or bleachout is determined by the pyrylium or thiapyrylium salt or salts present in the element. Neutral colored dye images are produced by using appropriate mixtures of two or more pyrylium and/or thiapyrylium salts. These salts may be incorporated in separate layers each containing an image promoting compound or coated together in a single layer with the image promoting compound.

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Support materials used to advantage in our elements include any of the supports used for photographic elements, such as paper, glass, cellulose acetate, cellulose nitrate, the polycarbonates, and other synthetic film-forming resins, coated with a layer of a material, such as, polyethylene, gelatin, etc. Silicated grained aluminum sheets are also used to advantage as a support. Wood, ceramics, stone and various metals are also used.

The pyrylium and thiapyrylium salts used to advantage in our elements include those represented by the formula:



wherein R_1 , R_2 and R_3 may each represent an aliphatic group having from 1 to 15 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl, isoamyl, hexyl, octyl, nonyl, dodecyl, 2,6-diphenylthia-4-pyramyridenemethyl, ethylene, styrylvinylene, styryl, alkoxystyryl, diethoxystyryl, dimethylaminostyryl, 1-butyl-4-p-dimethylaminophenyl - 1,3 - butadienyl, β -ethyl-4-dimethylaminostyryl; an alkoxy group such as methoxy, ethoxy, propoxy, butoxy, amyloxy, hexoxy, octoxy, etc.; aryl, such as phenyl, 4-biphenyl, 2,3,4,6-tetraphenyl, naphthyl, phenanthryl, phenylbenzo[b], an alkphenyl, such as 4-ethylphenyl, 4-propylphenyl, etc., alkoxyphenyl, 6-phenylhexatrienyl-(1,3,5), e.g., 4-ethoxyphenyl, 4-methoxyphenyl, 4-amyloxyphenyl, 2-hexoxyphenyl, 2-methoxyphenyl, 2-amyloxyphenyl, 3,4-dimethoxyphenyl, etc., acetoxypheyl, an ω -hydroxyalkoxyphenyl, e.g., 4-chlorocarbomethoxyphenyl, 2-hydroxyethoxyphenyl, 3-hydroxyethoxyphenyl, etc., 4-hydroxyphenyl, halophenyl, e.g., 3,4-dichlorophenyl, 3,4-dibromophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, etc., azidophenyl, nitrophenyl, etc., aminophenyl, e.g., 4-diethylaminophenyl, 4-dimethylaminophenyl, etc.; X is a hetero atom, such as oxygen, sulfur and selenium; and Y is an anionic function, such as, for example, perchlorate, fluoborate, nitrate, chloride, bromide, chloroaluminate, chloroferrate, sulfate, bisulfate, sulfacetate, methosulfate, alkanoates, such as acetate and especially trifluoroacetate, trichloroacetate, etc., aromatic sulfonates, such as p-toluene sulfonate, etc., anions from aromatic carboxylic acids, such as benzoate, and especially p-nitrobenzoate, 2,4-dinitrobenzoate, the trinitrobenzoates, etc.

In addition to the pyrylium and thiapyrylium salts described above, various other modifications can be made such as 2,3,4,6-tetra substituted derivatives, bis pyrylium and thiapyrylium salts, such as octamethylene-2,2'-bis-[4,6-di(4-methoxyphenyl)pyrylium fluoborate] and derivatives formed from a methyl substituted pyrylium salt and a cyclic ketone, such as 2,6-dimethyl-4-pyrone.

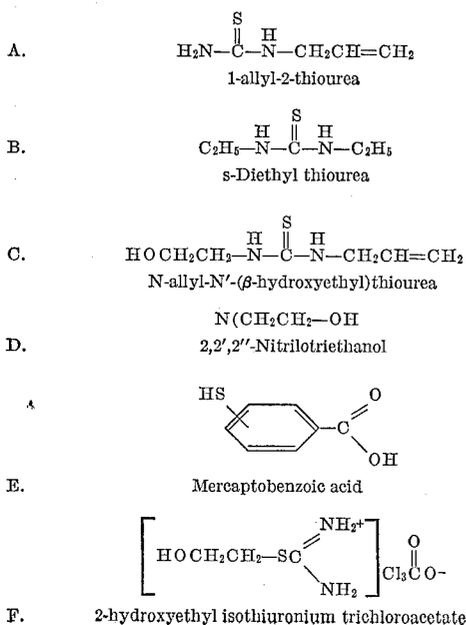
Included among the pyrylium and thiapyrylium salts

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that are used to advantage according to the invention are the following:

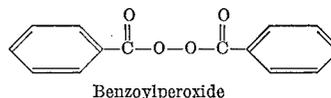
Compound Number	Name
1.....	2,4,6-triphenylpyrylium fluoroborate.
2.....	2,6-di-p-methoxyphenyl-4-phenylpyrylium fluoroborate.
3.....	2,6-di-p-methoxyphenyl-4-phenylthiapyrylium fluoroborate.
4.....	2,6-di-phenyl-4-p-methoxyphenylthiapyrylium fluoroborate.
5.....	2,6-di-p-ethylphenyl-4-methoxyphenylpyrylium fluoroborate.
6.....	2-(p-n-amyloxyphenyl)-4,6-diphenylthiapyrylium fluoroborate.
7.....	2-(p-amyloxystyryl)-4,6-diphenylpyrylium perchlorate.
8.....	2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium fluoroborate.
9.....	4,6-diphenyl-2-(styryl vinylene)pyrylium perchlorate.
10.....	4-p-acetoxystyryl-2,6-diphenylthiapyrylium fluoroborate.
11.....	2,3,4,6-tetraphenylpyrylium fluoroborate.
12.....	2-(p-methoxyphenyl)-4,6-diphenylthiapyrylium fluoroborate.
13.....	2-(p-methoxyphenyl)-4,6-diphenylpyrylium fluoroborate.
14.....	2,6-diphenyl-4-(o-methoxyphenyl)pyrylium fluoroborate.
15.....	2-(2-naphthyl)-4,6-diphenylpyrylium fluoroborate.
16.....	2-(1-naphthyl)-4,6-diphenylpyrylium fluoroborate.
17.....	2,3,4,6-tetraphenylthiapyrylium fluoroborate.
18.....	2,6-bis(4-chlorocarboxymethoxyphenyl)-4-phenylpyrylium fluoroborate.
19.....	2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium perchlorate.
20.....	2,6-di-m-nitrophenyl-4-p-nitrophenylpyrylium perchlorate.
21.....	2,4-di-p-methoxyphenyl-6-methoxystyryl pyrylium fluoroborate.
22.....	2,6-bis(p-ethylphenyl)-4-(p-pentoxystyryl)-thiapyrylium perchlorate.
23.....	2-(3,4-diethoxystyryl)-4,6-diphenyl pyrylium perchlorate.
24.....	4-(p-n-amyloxyphenyl)-2,6-bis(p-ethylphenyl)-thiapyrylium perchlorate.
25.....	4,6-diphenyl-2-styryl pyrylium perchlorate.
26.....	2-phenylbenzo(b)pyrylium ferric chloride.
27.....	7-hydroxy-4-(p-methoxystyryl)-2-phenylbenzo pyrylium pyrylium chloride.
28.....	4-(4-dimethylaminophenyl)-2,6-diphenyl pyrylium perchlorate.
29.....	2,4-bis(4-ethylphenyl)-6-(2,6-diphenyl thia-4-pyramyridenemethyl)pyrylium perchlorate.
30.....	2-[6-phenyl hexatrienyl-(1,3,5)]4,6-diphenyl pyrylium perchlorate.
31.....	2-(4-dimethylaminostyryl)-4,6-diphenylpyrylium sulfoacetate.

The image promoting compounds of our invention are sensitizers that make the pyrylium, thiapyrylium or selenopyrylium salts sensitive to light. The preferred sensitizers are compounds that contain a thiocarbonyl group, a mercapto group or a thioether group. Included among the sensitizers are the following representative compounds:



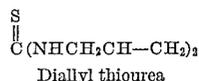
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- 10 The mixtures of the pyrylium salt(s), and/or thiapyrylium salt(s) and image promoting compound are dissolved advantageously for coating in any suitable solvents such as acetone, methoxyethanol, ethoxyethanol, methanol, hexanone, methylcellosolve acetate, ethylacetate, 15 toluene, xylene, chlorobenzene, trichloroethylene, methylenechloride, ethylenechloride, propylene chloride, etc., and various mixtures of these. In general any solvent can be used that will dissolve the image-forming compounds, e.g., the pyrylium, thiapyrylium or selenopyrylium salt 20 and the image-promoting compound, and the binder when a binder is used.

The binders used to advantage include any film forming material which is soluble in the solvents that dissolve the image-forming compounds. Included among these 25 binders are cellulose esters, e.g., ethyl-cellulose phthalate, cellulose acetate hydrogen phthalate, cellulose acetate with various amounts of free hydroxyl groups, etc.; phthalated polyvinyl acetals with varying amounts of phthalation; synthetic elastomers, e.g., polyvinyl toluene, styrene buta- 30 diene resin, copolymers of ethylacrylate and acrylic acid, etc.

The preferred binders are water-insoluble water-permeable materials such as cellulose acetate which is from 35 about 20 to about 35% acetylated, and cellulose acetate hydrogen phthalate.

The light-sensitive composition is coated to advantage on the support by any of the well known coating techniques used in coating photographic elements.

The coated and dried element is exposed to a light 40 image which, depending upon the particular materials in the light-sensitive layer, produces either a printout or a bleachout image. By a printout image we mean the formation of a colored image of a different color than the original coating. By a bleachout image we mean an image 45 formed by the bleaching of the dye in the original coating. We have found that neither a negative or a positive bleachout image reproduction of a positive original is obtained by controlling the exposure time; a negative image is produced by using a short exposure while a longer exposure 50 will produce a positive image.

After the printout or bleachout image is formed by exposure, it is stabilized to advantage by treating the light-sensitive layer with water, preferably warm water.

The following examples will serve to further illustrate 55 our invention.

Example 1

A light-sensitive coating composition having the general formulation:

60	Pyrylium or thiapyrylium salt	g--	0.5
	1-allyl-2-thiourea	g--	0.5
	Acetone	ml--	100

was prepared for each of the pyrylium and thiapyrylium salts identified in Table 1. A portion of each coating 65 composition was flow-coated on both polyethylene-coated paper and silicated, grained aluminum and dried under room conditions. Exposures were made to a 500-watt No. 2 RFL Photoflood bulb at a distance of 6 inches for 70 10 seconds through a negative transparency held in a contact exposure frame. The color of the printout image or bleachout image obtained for each coating is indicated in Table 1 along with the original color of the coating, the effect produced on the printout or bleachout image by 75 treatment with warm water and the color of the final image.

TABLE 1

Coating No.	Pyrylium or Thiapyrylium Compound No.	Original Color	Printout Color	Bleachout Color	Effect of Warm Water Treatment	Final Image
1	1	Yellow		Light yellow	Washes out nonexposed areas.	Light yellow on white background.
2	2	Red-orange		Light orange	do.	Light orange on white background.
3	3	Red		Light red	do.	Light orange on white background.
4	4	Orange		Light orange	do.	Medium orange on white background.
5	5	Yellow		Light yellow	do.	Light yellow on white background.
6	6	Red-orange		Light orange	do.	Orange on white background.
7	7	Orange	Gray		Nonexposed areas do not completely wash out.	Gray on yellow background.
8	8	Orange		Light orange	Fair washout.	Light orange on white background.
9	9	Red		Light red	Almost completely washed out.	Brown on white.
10	10	Orange	Excell. Purple on orange.		Does not develop out nonexposed areas.	Water turns entire coating purple; acid bleaches coating.
11	11	Yellow		White	Washes out nonexposed areas.	Yellow on white background.
12	12	Dark red-orange		Light orange	Does not wash out.	Light orange on dark orange background.
13	13	Red-orange		Light orange	Washes out nonexposed areas.	Orange on white background.
14	14	Pale orange		White		White on yellow-orange background.
15	15	Orange-yellow	Dark orange		Nonexposed areas are washed out.	Light orange on white background.
16	16	Orange-yellow	Dark orange		do.	Do.
17	17	Yellow		Very slight	Nonexposed areas are washed out.	Good yellow on white background.
18	18	Orange	Deep orange		Washes out nonexposed areas.	Orange on white background.
19	19	Orange		Light orange	do.	Orange on white background.

The coatings made on the silicated grained aluminum supports were swabbed with a commercial desentizing etch after the warm-water treatment, then the swabbed coatings were hand-inked with commercial lithographic developing ink. Coatings 1, 3, 4, 5, 6, 7, 8, 13, 15, 16, 17 and 19 were found to be ink receptive.

Coatings made of the compositions in which S-diethylthiourea is substituted for 1-allyl-2-thiourea give similar results.

Example 2

A light-sensitive coating composition made by dissolving 0.5 g. of 2-(p-amyloxystryl)-4,6-diphenylpyrylium perchlorate and 0.5 g. of N-allyl-N'-(β -hydroxyethyl)-thiourea in 100 ml. of acetone was flow-coated on polyethylene coated paper and dried. The light magenta colored coating was exposed imagewise to a 35 amp. arc at a 3-foot distance for 15 seconds. The exposed areas were readily bleached. On subsequent treatment with dilute

hydrochloric acid a stable positive print was obtained. Water can also be used to stabilize the image.

Example 3

A light-sensitive coating composition having the general formulation:

Pyrylium or thiapyrylium salt	g	0.5
Image promoting compound	g	0.5
Acetone	ml	100

was prepared for each of the pyrylium or thiapyrylium salts and image promoting compounds listed in Table 2. A portion of each coating composition was flow-coated on polyethylene-coated paper and dried for 1 minute at 40° C. Samples were exposed for 1 minute at a 3-foot distance from a 35-amp. carbon arc. The original color of the coating, the color of printout or bleachout image, effect of treatment of print with warm water and the color of final print image are recorded in Table 2.

TABLE 2

Coating No.	Pyrylium or Thiapyrylium Salt No.	Image Promoting Compound	Original Color of Coating	Printout Color	Bleachout Color	Effect of Warm Water on Print	Final Image
1	13	None	Red-orange			No color visually present.	None.
2	13	A	do.		Strong bleach	Nonexposed areas became visually clear.	Fairly strong image on clear background.
3	22	A	Bright orange		Slight bleach	Image turned brown, clear background.	Brown colored image.
4	22	D	Yellow-orange		do.	No effect.	No visual effect on original bleach-out.
5	22	F	do.	Light brown		do.	No visual effect on original print-out.
6	22	E	do.	Weak brown		No change.	Weak brown image remains.

The following example illustrates how by controlling the exposure time either a negative or a positive bleachout image can be made of a positive transparency.

Example 4

A composition containing 1/2% by weight of 2-(p-amyloxystyryl)-4,6-diphenyl pyrylium perchlorate, 1/2% by weight of 1-allyl-2-thiourea in acetone was flow-coated on polyethylene-coated paper stock and dried. One sample of this coating was exposed to a positive image in a Bruning Copyflex 110 Office Copying Machine at 12 ft./min. then treated with water to produce a good magenta dye negative reproduction of the original. Another sample of this coating was given the same treatment but exposed at 1 ft./min. instead of 12 ft./min. to produce a good magenta dye positive reproduction of the original image. A study of the image reproduction of a resolving power chart showed that the image reproduced approximately 50 lines per millimeter.

The following example will illustrate how our light-sensitive coating composition is dispersed in a water-insoluble water-permeable binder and coated to produce an element that will reproduce an image having more than 565 lines per millimeter.

Example 5

A coating composition containing 0.5 g. of 2,4-diphenyl-6-(3,4-diethoxyethyl)pyrylium perchlorate, 10.0 g. of 1-allyl-2-thiourea, 10.0 g. cellulose acetate with about 32.5% acetyl content all dissolved in 79.5 g. of a 1:1 mixture of acetone and methoxyethanol was coated on a gel-subbed cellulose acetate support and dried. A sample of this coating was exposed to activating radiation through the image of a resolving power chart. The exposed material was treated with water. The resulting print was found to have reproduced an image having more than 565 lines per millimeter.

Example 6

Coating compositions containing 2 1/2% by weight of N-allyl-N'-(beta-hydroxyethyl)thiourea, 5% by weight of cellulose acetate with about 32.5% acetyl content in a 1:1 mixture of acetone-methoxyethanol and 1/4% by weight of the pyrylium or thiapyrylium salts indicated in Table 3 were coated on a suitable transparent support and dried. The results obtained by exposing samples of these coatings to an original image in a Bruning Copyflex 100 Diazo Copy Machine at the ft./min. indicated, are summarized in Table 3.

TABLE 3

Coating No.	Pyrylium or Thiapyrylium Salt No.	Exposure Rate in ft./min.	Final Positive Image Produced
1	23	12	Faint magenta.
2	24	1/2	Bright yellow.
3	25	4	Light yellow.
4	26	4	Heavy cyan.
5	27	5	Orange-red.
6	28	1	Magenta.
7	29	1/2	Heavy cyan.
8	30	4	Brownish magenta.
9	31	1/2	Heavy green.
10	9	10	Light red.

The bleachout was enhanced by substituting N-allyl-N'-(beta-hydroxyethyl)thiourea for 1-allyl-2-thiourea, and was also enhanced by increasing the ratio of the allyl-thiourea to the pyrylium (or thiapyrylium) salt.

Example 7

Coatings were made on a suitable support, of compositions containing 1/4% by weight of 2-(3,4-diethoxystyryl)-

4,6-diphenyl pyrylium perchlorate and N-allyl-N'-(beta-hydroxyethyl)-thiourea at each of the following percents by weight: 1/4, 3/4, 1 1/4 and 2 1/4. Each of the 4 dried coatings was exposed to an original image for 1 minute using a Signet B Verifax Copier. The magenta image produced was found to show more bleachout as the percent of the thiourea compound in the composition was increased.

A similar coating was made of a composition in which benzoyl peroxide was substituted for N-allyl-N'-(beta-hydroxyethyl)thiourea which produced a bleachout image.

Example 8

A coating made on a suitable support of a composition containing 1/2% 2-(3,4-diethoxystyryl)-4,6-diphenyl pyrylium perchlorate and 1% N-allyl-N'-(beta-hydroxyethyl) thiourea was dried, image exposed, water-treated, dried and placed over a fluorescent light source for 16 days. One-half of the magenta dye image was protected from the light during the exposure time. A comparison of the two halves of the print showed substantially no fading of the magenta image, however the slight yellowish background seen in the protected half was essentially clear in the exposed half.

Three colored images are produced by combining differently colored images, such as cyan, magenta and yellow, or red, blue and green, or magenta and green, or red and cyan, etc. These differently colored images may be made in separate layers on transparent supports which are superimposed in registration to produce the neutral image, or the required color forming systems are coated in a single layer on a support or in separate layers on a support.

The following example will illustrate.

Example 9

A coating composition was made containing the following material:

Cellulose acetate	-----g--	1
N-allyl-N'-beta-hydroxyethyl thiourea	-----g--	0.75
2-phenylbenzo[b]pyrylium ferric chloride	-----g--	0.207
4,6-diphenyl-2(3,4 - diethoxystyryl)pyrylium perchlorate	-----g--	0.017
4,6-diphenyl-2-styrylpyrylium perchlorate	-----g--	0.014
1:1 methoxyethanol:acetone	-----cc--	10

Portions of this composition were flow-coated on clear acetate support and on polyethylene coated paper. Each element after drying was exposed to a #2 Photoflood lamp at 12 inches for 1 1/2 minutes through a transparency having a three-color picture. In each of our elements a three-color print was produced of the original multi-color slide. The color prints were then stabilized by treating with water.

Similarly, other pyrylium or thiapyrylium salts can be used in mixtures in our elements to produce three-color prints. For this purpose salts are selected which when used together in the proper proportions in a light-sensitive layer in our element, will produce upon exposure a neutral reproduction of a neutral original image.

The light-sensitive elements described in the preceding examples are used to advantage for many copying purposes, such as copying documents, or microfilm copies of the documents, making prints from photographic negatives, color transparencies, etc., making corrective masks for photographic printing operations, etc.

Another use is for making photographic templates on material such as metal stock, wood, plastics, glass, ceramics, stone, etc., as a guide for such operations as cutting, milling, drilling, etc. This is illustrated as follows.

Example 10

A coating composition containing 0.2 g. of 4,6-diphenyl-2-(3,4-diethoxystyryl)pyrylium perchlorate, 0.25

g. of N-allyl-N'-(β -hydroxyethyl)thiourea, and 5.0 g. of cellulose acetate dissolved in 100 ml. of 1:1 methoxyethanol acetone mixture was flow coated on a piece of aluminum and dried. Another sample was prepared by brushing the light-sensitive coating on. An image-wise exposure of two minutes to a 35 amp arc at 3 feet produced a good positive magenta image of the original. This was stabilized by water treatment.

We have found that images produced in many of our elements as described will produce fluorescent images upon irradiation with ultraviolet light.

For example, a print made by exposing an element having a layer containing 2,3,4,6-tetraphenylpyrylium fluoroborate to a Photoflood RFL No. 2 lamp for 6 seconds at 10 inches through an image was found to fluoresce strongly in areas that had been exposed to the tungsten source. Prior to tungsten light exposure the coating gave only a very slight fluorescence.

Another element with a layer containing a mixture of 2-(1-naphthyl)-4,6-diphenylpyrylium fluoroborate and allylthiourea gave a steel-blue printout image when exposed to a Photoflood RFL No. 2 lamp for 10 seconds at 6 inches through an image. After treatment with warm water, the blue color changed to yellow while the visual color of the unexposed area disappeared. Under ultraviolet radiation the unexposed regions fluoresced a bright yellow-orange. The same result was obtained by using the thiaanalogue of this pyrylium salt.

The pyrylium and thiapyrylium salts used to illustrate the invention were prepared in general by the methods described in copending Van Allan, Natale, and Rauner U.S. Ser. No. 146,743, filed Oct. 23, 1961, now U.S. Patent No. 3,250,615.

Compounds 1 and 4 were prepared as described in *Helv. Chim. Acta.* 39, 13 (1956).

Compound 2 was prepared by condensing p-methoxyacetophenone with benzaldehyde in the presence of boron trifluoride etherate. Compound 3 was prepared by treating compound 2 with sodium sulfide.

Compound 5 was prepared by condensing one molar equivalent of 4-methoxybenzaldehyde with two molar equivalents of 4-ethylacetophenone in the presence of boron trifluoride etherate.

Compounds 6, 8 and 23 were prepared as described by Van Allan, Natale and Rauner.

Compound 7 was prepared by condensing 2-ethyl-4,6-diphenylpyrylium perchlorate with 4-amyloxybenzaldehyde.

Compound 9 was prepared by condensing 4,6-diphenyl-2-methylpyrylium perchlorate with cinnamoylaldehyde.

Compound 10 was prepared by condensing acetophenone with p-acetoxy benzaldehyde in the presence of boron trifluoride etherate and treating the product with sodium sulfide, M.P. 278-280° C.

Compound 11 was prepared by condensing chalcone with desoxybenzoin in the presence of boron trifluoride etherate, M.P. 230° C.

Compounds 12 and 13 were prepared like the corresponding thiapyrylium perchlorate and pyrylium perchlorate as described in Van Allan, Natale and Rauner but using boron trifluoride etherate as the condensing agent.

Compound 14 was prepared by condensing one molar equivalent of 2-methoxybenzaldehyde with two molar equivalents of acetophenone in the presence of boron trifluoride etherate.

Compound 15 was prepared by condensing benzalacetophenone with 2-naphthylaldehyde in the presence of boron trifluoride etherate, M.P. 270° C.

Compound 16 was prepared like 15 but by using 1-naphthylaldehyde, M.P. 265° C.

Compound 17 was prepared by treating compound 11 with sodium sulfide.

Compound 18 was prepared by condensing p- β -carboxymethoxyacetophenone with benzaldehyde in the presence

of boron trifluoride etherate and heating the product with thionyl chloride, M.P. 120° C.

Compound 19 was prepared from the corresponding fluoroborate described by Van Allan, Natale and Rauner by metathesis with perchloric acid.

Compound 20 was prepared by treating compound 1 with nitric acid and treating the product with phosphorous oxychloride, M.P. >300° C.

Compound 21 was prepared by condensing p-methoxyacetophenone with p-methoxybenzaldehyde in the presence of sodium hydroxide and then treating the product with boron trifluoride etherate, M.P. 285° C.

Compound 22 was prepared by condensing 4-pentoxybenzaldehyde with 4-ethylacetophenone in the presence of phosphorous oxychloride and reacting the product with sodium sulfide.

Compound 24 was prepared by condensing 4-amyloxybenzaldehyde with 4-ethylacetophenone in the presence of perchloric acid and treating the product with sodium sulfide.

Compound 25 was prepared by condensing 6-methyl-2,4-diphenylpyrylium perchlorate with benzaldehyde.

Compound 26 was prepared by condensing salicylaldehyde with acetophenone in the presence of boron trifluoride and ferric chloride, M.P. 110° C.

Compound 27 was prepared by condensing resorcinol with benzoylacetone in the presence of saturated HCl and heating the product with anisaldehyde, M.P. 263° C.

Compound 28 was prepared by condensing p-dimethylaminobenzaldehyde with acetophenone in the presence of sulfuric acid and treating the product by pouring it into alcohol containing perchloric acid, M.P. 335° C.

Compound 29 was prepared by reacting p-ethylacetophenone with acetic anhydride and condensing the product with 2,6-diphenyl-thia-4-pyrone in the presence of perchloric acid, M.P. 180° C.

Compound 30 was prepared by condensing 4-formyl-1-phenyl-2,4-butadiene with acetophenone in the presence of boron trifluoride etherate and then treating with perchloric acid.

Compound 31 was prepared by condensing acetophenone with dimethylaminobenzaldehyde in the presence of acetic anhydride and sulfuric acid.

The image promoting agents A, B, C, D, G and H are well known compounds. Image promoting compound F, 2-hydroxyethylisothiuronium trichloroacetate, was prepared as follows. Four moles of 2-chloroethanol and one mole of thiourea were placed in a one-liter flask and mechanically stirred at between 35° to 50° C. for 105 hours. The resulting solution was cooled and the white crystalline product precipitated with one liter of diethyl ether, and recrystallized from ethanol. From 0.05 mole of the 2-hydroxyethylisothiuronium chloride thus produced and 0.06 mole of trichloroacetic acid converted to its potassium salt, was obtained 10.9 g., M.P. 124° dec. of compound F.

The printout or bleachout elements of our invention are valuable for use in making copies of documents, pictures, etc. in neutral tones or in various colors. The element comprises a support coated with a solution of one or more pyrylium, thiapyrylium or selenopyrylium salts, an image promoting compound with or without a binder. The preferred elements having a binder reproduce an image having more than 565 lines per millimeter. The image formed is stabilized by rinsing the element in water.

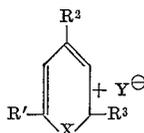
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A light-sensitive photographic element comprising a support having coated thereon at least one layer comprising a mixture of:

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- (1) at least one image-forming compound selected from those having the formula:



wherein R', R² and R³ each represent a group selected from the class consisting of an aliphatic group, an alkoxy group, and an aryl group; X is a heteroatom selected from the class consisting of the oxygen atom, the sulfur atom and the selenium atom; and Y is an anionic function;

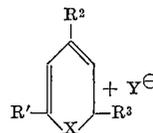
- (2) at least one sensitizing compound that contains a group selected from the class consisting of thiocarbonyl, mercapto, carbonyl peroxide and thioether; and
- (3) a water-insoluble water-permeable organic colloidal binder material.
2. A light-sensitive photographic element of claim 1 in which the sensitizing compound is 1-allyl-2-thiourea.
3. A light-sensitive photographic element of claim 1 in which the sensitizing compound is diallylthiourea.
4. A light-sensitive photographic element of claim 1 in which the sensitizing compound is s-diethyl thiourea.
5. A light-sensitive photographic element of claim 1 in which the sensitizing compound is N-allyl-N'-(β-hydroxyethyl)-thiourea.
6. A light-sensitive photographic element of claim 1 in which the sensitizing compound is mercaptobenzoic acid.
7. A light-sensitive photographic element of claim 1 in which the sensitizing compound is 2-hydroxyethyl isothiuronium trichloroacetate.
8. A light-sensitive photographic element of claim 1 in which the sensitizing compound is benzoylperoxide, and the layer comprising a mixture of items (1), (2) and (3) of claim 1 is the sole light-sensitive layer.
9. A light-sensitive photographic element of claim 1 in which the sensitizing compound is 2,2',2''-nitrotriethanol and the layer comprising a mixture of items (1), (2) and (3) of claim 1 is the sole light-sensitive layer.
10. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 2-(3,4-diethoxystyryl)-4,6-diphenyl pyrylium perchlorate, N-allyl-N'-(β-hydroxyethyl)thiourea as the sole light-sensitive component and cellulose acetate.
11. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 2-(p-amyloxyphenyl)-2,6-bis(p-ethylphenyl)thiapyrylium perchlorate, N-allyl-N'-(β-hydroxyethyl)thiourea as the sole light-sensitive component and cellulose acetate.
12. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 4,6-diphenyl-2-styryl pyrylium perchlorate, N-allyl-N'-(β-hydroxyethyl)thiourea as the sole light-sensitive component and cellulose acetate.
13. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 2-phenylbenzo[b]pyrylium ferric chloride, N-allyl-N'-(β-hydroxyethyl)-thiourea as the sole light-sensitive component and cellulose acetate.
14. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 2-[6-phenylhexatrienyl-(1,3,5)]-4,6-diphenyl pyrylium perchlorate, N-allyl-N'-(β-hydroxyethyl)thiourea as the sole light-sensitive component and cellulose acetate.
15. A light-sensitive photographic element comprising a support having coated thereon a composition comprising 4-(p-n-amyloxyphenyl)-2,6-bis(p-ethylphenyl)thiapyrylium perchlorate, 2-phenylbenzo[b]pyrylium ferric chloride, 2-[6-phenylhexatrienyl(1,3,5)]-4,6-diphenyl

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pyrylium perchlorate, and N-allyl-N'-(β-hydroxyethyl)thiourea as the sole light-sensitive component.

16. A light-sensitive coating composition comprising:

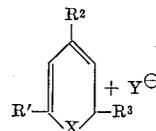
- (1) at least one image-forming compound selected from those having the formula:



wherein R', R² and R³ each represents a group selected from the class consisting of an aliphatic group, an alkoxy group, and an aryl group; X is a heteroatom selected from the class consisting of the oxygen atom, the sulfur atom and the selenium atom; and Y is an anionic function;

- (2) at least one sensitizing compound that contains a group selected from the class consisting of thiocarbonyl, mercapto, carbonyl peroxide and thioether;
- (3) a water-insoluble water-permeable organic colloid binder; and
- (4) at least one organic solvent in which the said items (1), (2) and (3) are soluble.
17. A light-sensitive coating composition of claim 16 in which the water-insoluble water-permeable organic colloid binder is cellulose acetate.
18. A light-sensitive photographic element comprising a support having coated thereon at least one layer comprising a mixture of:

- (1) at least one image-forming compound selected from those having the formula:

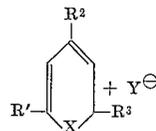


wherein R', R² and R³ each represents a group selected from the class consisting of an aliphatic group, an alkoxy group, and an aryl group; X is a heteroatom selected from the class consisting of the oxygen atom, the sulfur atom and the selenium atom; and Y is an anionic function; and

- (2) at least one sensitizing compound that contains a group selected from the class consisting of thiocarbonyl, mercapto, carbonyl peroxide and thioether.
19. A light-sensitive element of claim 18 in which the sensitizing compound is selected from the class consisting of 1-allyl-2-thiourea, s-diethyl thiourea, N-allyl-N'-(β-hydroxyethyl)-thiourea, 2,2',2''-nitrotriethanol, mercaptobenzoic acid, 2-hydroxyethyl, isothiuronium trichloroacetate, benzoylperoxide and diallyl thiourea.
20. A process for making a photographic image comprising the steps:

- (1) exposing to a light image a light-sensitive layer comprising a mixture of:

- (a) at least one compound selected from those having the formula:



wherein R', R² and R³ each represents a group selected from the class consisting of an aliphatic group, an alkoxy group, and an aryl group; X is a heteroatom selected from the class consisting of the oxygen atom, the sulfur atom and the selenium atom; and Y is an anionic function;

- (b) at least one sensitizing compound that contains a group selected from the class consisting of thiocarbonyl, mercapto, carbonyl peroxide and thioether, and

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- (c) a water-insoluble water-permeable organic colloidal binder material; and
 (2) stabilizing the image formed in step (1) by treating the said light-sensitive layer with water.

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10 NORMAN G. TORCHIN, *Primary Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,300,314 Dated January 24, 1967

Inventor(s) Frederick J. Rauner and Conrad G. Houle

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, line 42 delete the term "nitrolotri-" and substitute in its place ---nitrilotri- ---.

Column 12, line 52, delete the "," between "2-hydroxyethyl" and "isothiuronium".

**SIGNED AND
SEALED
JAN 20 1970**

(SEAL)

Attest:

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Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents